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Japanese Patent Application JP 53 – 53634 A

Title: Method for the Purification of Terephthalic Acid

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(54) Title of the Invention: **Method for Producing High-Purity Terephthalic Acid**

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2, Nihonbashi-Muromachi 2 chome, Chuo-ku, Tokyo-toSPECIFICATION**1. Title of the Invention**

15 Method for Producing High-Purity Terephthalic Acid

2. Claims

A method for producing high-purity terephthalic acid as a result of oxidizing p-xylene with molecular oxygen-containing gas in an acetic acid solvent in the presence of an oxidation catalyst and accelerator, separating the resulting terephthalic acid from the reaction liquid, and

20 then washing this terephthalic acid with acetic acid solvent, wherein said method is characterized in that the acetic acid fraction is recovered and reused by means of vaporizing and condensing

the washing solution used in the washing procedure, the insoluble matter that has precipitated in the liquid residue is subjected to solid-liquid separation, essentially all of the solid matter is discharged from the system, and the remaining liquid components are recovered and reused.

3. Detailed Description of the Invention

5 (Field of Industrial Utilization)

The present invention relates to a method for producing high-purity terephthalic acid (TPA hereafter) suitable for producing polyester, and in particular, to a method for producing high-purity TPA by means of washing crude TPA product with acetic acid, removing the impurities contained in the washing liquid, and efficiently reusing the unreacted components,
10 acetic acid, residual catalyst, and other useful substances.

Attention has been focused in recent years on so-called direct polymerization whereby TPA is directly polymerized with a glycol as a substitute for the method whereby polyester is produced via a step in which TPA is esterified and converted to dimethyl terephthalate, which is easier to purify. This has been accompanied by an increased demand for high-quality TPA.

15 Methods whereby bromine compounds (JP (Kokoku) 34-2666), ketones (JP (Kokoku) 40-2539), paraldehydes (JP (Kokoku) 40-13856 and 46-7935)), acetaldehydes (JP (Kokoku) 40-24180), and certain other additives other than metal catalysts are used as accelerators are well known as processes for producing benzene carboxylates with the help of the liquid-phase oxidation of dialkylbenzenes. Methods that use these types of additives are very effective for
20 producing benzene dicarboxylates, but in addition to the resulting TPA and unreacted p-xylene, the p-xylene oxidation reaction system contains 4-carboxybenzaldehyde, paratoluic acid, and other intermediate products, as well as cobalt, manganese, chromium, iron, and other catalysts; organic byproducts that become the source of discoloration; and the like. These substances must be removed by means of washing with the same acetic acid that is used as the oxidation solvent
25 in order to purify the TPA. The washing liquid that is used for washing thus contains all of these intermediate products and other substances, and recovery and reuse of these substances represent a major industrial problem.

Acetic acid is reused for washing as a result of first vaporizing (or vaporizing and condensing) this washing liquid. The residues (vaporizer bottoms) have been treated with the help of the following methods (1) through (3) in an attempt to solve the above-mentioned problem.

- 5 (1) Circulation of the entire amount to the reaction system
 (2) Discharge of the entire amount from the system
 (3) Discharge of the catalyst component of the bottom product from the system after
recovery

10 However, method (1) has a problem in that impurities accumulate in the reaction system to contaminate the TPA; therefore, high-purity TPA is not obtained.

15 The problem associated with method (1) does not occur with method (2), but when all of the TPA is discharged from the system, it is necessary to maximize condensation of the bottoms in order to reduce the amount of accompanying acetic acid as much as possible. However, large amounts of TPA precipitate to form highly viscous slurry that is difficult to handle when the condensation rate is raised. On the other hand, a large amount of acetic acid is lost when the optimal slurry viscosity is maintained. Another undesirable result is that it becomes necessary to treat the large amounts of residue that are generated. Discharging all of the untreated bottoms from the system is not an economic method because the vaporizer bottoms contain large amounts of catalyst components.

20 Method (3) is not necessarily preferred because a catalyst recovery facility is needed and a complex procedure is required. There is also a disadvantage in that large volumes of residue are generated, and the like.

25 The inventors performed intense studies in order to overcome the above-mentioned disadvantages of prior art and, as a result, completed the present invention, which is described below.

That is, the present invention is a method for producing high-purity terephthalic acid as a result of oxidizing p-xylene with molecular oxygen-containing gas in an acetic acid solvent in the presence of an oxidation catalyst and accelerator, separating the resulting terephthalic acid

from the reaction liquid, and then washing this terephthalic acid with acetic acid solvent, wherein the method is characterized in that the acetic acid fraction is recovered and reused by means of vaporizing and condensing the washing solution used in the washing procedure, the insoluble matter that has precipitated in the liquid residue is subjected to solid-liquid separation, essentially all of the solid matter is discharged from the system, and the remaining liquid components are recovered and reused.

The oxidation catalyst used in the present invention is selected from compounds of cobalt, manganese, chromium, iron, and the like, and the reaction accelerator is selected from bromine compounds, ketones, paraldehydes, acetaldehydes, and the like. Air is normally used as the molecular oxygen-containing gas. A conventional solid-liquid separator is used to separate the resulting terephthalic acid from the reaction liquid.

The quality of the crude TPA, that is, the number of times the TPA is washed with acetic acid, the washing temperature, the ratio of solvent and TPA during washing, and other washing conditions, are determined by the desired quality of the high-purity TPA. However, it is preferred that washing be performed at a temperature that is the boiling point of the acetic acid or higher in order to remove the 4-carboxybenzaldehyde or the colored component contained in the crude TPA. When the crude TPA is washed at a temperature that is the boiling point of acetic acid or higher, it is preferred that the slurry after washing be cooled to the boiling point or lower as gradually as possible in order to improve the effect of the washing. It is particularly effective to subject the slurry after washing to solid-liquid separation at a temperature that is higher than the boiling point.

Although the effect of washing improves with an increase in the number of days of washing¹, the catalyst contained in the crude TPA is washed away relatively easily when compared to the 4-carboxybenzaldehyde, and the TPA in the final steps of multistep washing therefore contains virtually no catalyst component. In this case as well, there are limits to the condensation of the vaporizer bottoms and there is an increase in the loss of acetic acid and the production of the residue when the bottoms of solvent used in the final steps of washing are

¹ Amended to read as indicated in item (1) of the Procedural Correction.

discharged from the system without further treatment, so it is preferable to use the method of the present invention.

Distillation, vaporization, or another method can be used to condense the used washing solvent of the present invention, and the condensation temperature is preferably 160°C or less.

5 Moreover, any type of vaporizer and any method for solid-liquid separation of the bottoms after condensation can be used.

The used solvent condensation percentage, which is equal to the amount of used solvent divided by the amount of bottoms, can be selected as needed from a range within which the slurry can be handled, but if the condensation rate is too low, (1) the solids content of the
10 vaporizer bottoms will also be low, impurities will be discharged to outside the reaction system, and condensation will have a small effect; (2) the amount of circulating liquid will be high and there will be excess acetic acid in the reaction system when the recovered liquid components are recirculated to the oxidation reaction; and (3) a large amount of TPA will precipitate and the resulting slurry will be difficult to handle when the recovered liquid components are further
15 vaporized and used as a washing solvent. Consequently, the amount of solids in the bottoms increases with increased condensation rate, and although the effect of removing impurities will be enhanced, normal operation of the vaporizer will be difficult because the slurry viscosity of the bottoms will increase. Consequently, a distillation (vaporization) condensation rate of 3 to 60 is preferred in order to effectively conduct the present invention. The acetic acid fraction
20 recovered at this time is reused as a washing liquid.

The impurities can then be removed as a result of subjecting the precipitate that has formed in the residue (bottoms) to solid-liquid separation and discharging essentially the entire solid fraction from the system. Moreover, the liquid components that have been separated are circulated to the oxidation system, but it is more effective to re-condense part of the liquid,
25 circulate the fraction as washing liquid, and discharge the remainder from the system at this time. That is, separation of solids from the vaporizer bottoms will facilitate additional condensation of the liquid components, markedly reduce the amount of residue that is discharged from the system, and reduce the accompanying loss of acetic acid. In addition, the most effective operation can be performed as a result of primarily removing colored components as solid

components (because these components degrade the quality of the TPA), and separately discharging as liquid components substances that are readily soluble in the acetic acid solvent and that interfere with the reaction. The ratio of the portion of the liquid components of the vaporizer bottoms that is circulated to the reaction system and the portion that is re-condensed is
5 determined by balancing catalyst loss, the amount of impurities discharged from the reaction system, and the accompanying change in the quality of TPA in the reaction system, but between 50% and 97% is usually circulated to the reaction system. Moreover, it is not always necessary to continuously perform these operations, and they can be performed using a batch system.

Condensation of liquid components in the bottoms can be accomplished using any type of
10 vaporizer, and the filtrate separated in a solid-liquid separator can be circulated to the first vaporizer. Incineration and other waste treatments can be performed on the cake component in the bottoms that has been subjected to solid-liquid separation. However, this cake is primarily TPA; therefore, it can also be used as a dimethyl terephthalate starting material in untreated or treated form. The condensed residue discharged from the system can be incinerated, or the
15 catalyst component can be further recovered from this liquid.

Figure 1 is a diagram showing a case in which acetic acid recovered by means of evaporation after washing TPA is recirculated as a washing liquid, and a portion of the liquid components recovered from the solid-liquid separator is circulated to the reaction vessel; another portion is re-condensed and the residue is sent to the washing vessel; and the remainder is
20 discharged from the system. The flow of the TPA production steps will be described while referring to this figure.

P-xylene, a catalyst, an accelerator, and the like are fed from tubing 1, air for oxidation is fed from tubing 2, and TPA is produced by a reactor 3. The resulting TPA slurry is fed through tubing 4 to a separator 5. The filtrate is subjected to dehydration or the like (not shown), and
25 then the cake that has been separated with the help of a separator 5 and will be circulated through tubing 21 to the reactor enters a slurry washing vessel 7 through tubing 6. The washing solvent is introduced to the slurry washing vessel through tubing 16, and the TPA is washed.

The washed slurry is fed through tubing 8 to a separator 9, and the separated TPA is passed through tubing 10 and dried by a dryer 11.

Meanwhile, the used washing liquid is fed through tubing 12 to a first vaporizer 13. The vapor that is produced as a result of evaporation in the first vaporizer 13 enters a condenser 15 through tubing 14 and is condensed. This product is reused as a washing liquid. The first vaporizer bottoms are fed through tubing 17 to a separator 18. The solid component is discharged from the system. The filtrate is passed through tubing 19. Part of the filtrate is then passed through tubing 20, circulated to the reaction system, and used in the operation. The remaining filtrate enters a second vaporizer 23 and is further condensed. The vapor produced as a result of vaporization enters a condenser 15 through tubing 24 and is reused as a washing liquid. The second evaporator bottoms are discharged from the system as a residue 23.

The present invention will now be described in specific terms with working examples. The "parts" in the working examples represents parts by weight, and alkali transmissivity represents a measure of TPA purity. Alkali transmissivity was determined by means of dissolving 7.5 g of terephthalic acid in 50 mL of a 2N potassium hydroxide solution and then measuring transmissivity at 340 m μ with a spectrophotometer. The colored impurity content of the terephthalic acid is a relative value.

Reference Example

A mixture of 18 parts of p-xylene, 0.75 part of cobalt acetate, 1.25 parts of water, 9 parts of paraldehyde, and 71 parts of acetic acid was fed to a reactor equipped with a rotary agitator, and the ingredients were reacted by being continuously brought into contact with air blown from the bottom of the reaction vessel at a reaction pressure of 5 kg, a reaction temperature of 130°C, and an average holding time of four hours.

The product obtained from the reactor was subjected to solid-liquid separation, and the resulting TPA was washed with acetic acid containing approximately 10% of water. The amount of washing liquid was 120 parts, the washing temperature was 160°C, and the washing time was 1 hour. When the TPA after washing was subjected to solid-liquid separation and the alkali transmissivity of the TPA was measured, the result was 83%.

Working Example 1

First, 120 parts of the washing filtrate obtained in the reference example were subjected to simple distillation at normal pressure. Then the distillate was reused to wash the cake. The

bottoms were condensed to 6 parts and subjected to solid-liquid separation. There was approximately 0.2 part of solids. Of the 5.8 parts of filtrate, 0.6 part was further condensed to 0.03 part. The fraction was reused to wash the cake. The remaining 5.2 parts were added to the oxidation reactor discussed in the Reference Example and reacted under the same conditions as in the reference example. When the procedure was repeated ten times, after 65.8 parts of the liquid from the reactor slurry that had been separated into solid and liquid fractions and then dehydrated, was added in place of the 71 parts of fresh acetic acid, the quality of the TPA product had all but stabilized, and the alkali transmissivity was 76%.² The cobalt acetate loss per one day³ was 0.005 part.

10 **Comparative Example 1**

The total amount of bottoms in Working Example 1 was added to the oxidation reactor in the reference example and reacted under the same conditions as in the working example. The alkali transmissivity of the TPA product when this procedure was repeated ten times was 50%.

Working Example 2

15 The entire 5.8 parts of liquid components obtained as a result of subjecting the bottoms to solid-liquid separation in Working Example 1 was added to the oxidation reactor used in the reference example and reacted under the same conditions as described in the Working Example. The alkali transmissivity of the TPA product after repeating the above-mentioned procedure 14 times was 70%.

20 **Comparative Example 2**

Six parts of bottoms in the working example were further condensed without being treated in order to be discharged from the system, the material was difficult to handle when condensed to 1 part or less, and the amount of filtrate was at least three times the amount stated in Working Example 1. Cobalt acetate loss per cycle at this time was approximately 0.5 parts.

² Amended to read as indicated in item (2) of the Procedural Correction.

³ Amended to read as indicated in item (3) of the Procedural Correction.

4. Brief Description of the Drawings

Figure 1 is a schematic drawing showing the flow of the present invention. The numbers in the figures represent the following.

- | | | |
|----|-------------------------------------|--------------------------------|
| | 1. Feed tube | 2. Air tube |
| 5 | 3. Oxidation reactor | 4. Reaction liquid tubing |
| | 5. Solid-liquid separator | 6. Slurry tubing |
| | 7. Washing machine ⁴ | 8. Post-washing slurry tubing |
| | 9. Solid-liquid separator | 10. Product tubing |
| | 11. Product dryer | 12. Used washing liquid tubing |
| 10 | 13. Vaporizer | 14. Vapor tubing |
| | 15. Condensing machine ⁵ | 16. Washing liquid tubing |
| | 17. Bottoms tubing | 18. Solid-liquid separator |
| | 19. Filtrate tubing | 20. Circulated filtrate tubing |
| | 21. Filtrate tubing | 22. Filtrate tubing |
| 15 | 23. Vaporizer | 24. Vapor tubing |
| | 25. Solid residue | |

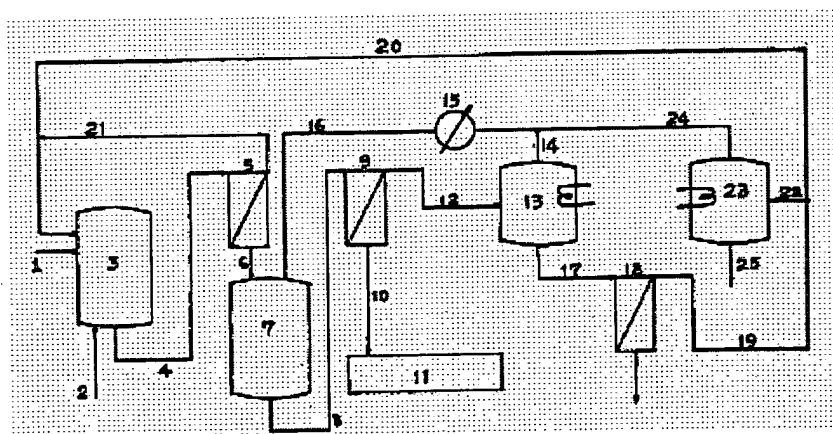


Fig. 1

⁴ Amended to read as indicated in item (4) of the Procedural Correction.

⁵ Amended to read as indicated in item (5) of the Procedural Correction.

Description of Amendment Pursuant to Article 17(2) of the Patent Law

Following is an amendment filed pursuant to Article 17(2) of the Patent Law regarding Japanese Patent Application 51-127323 (JP (Kokai) 53-53634, published in Unexamined Patent Gazette 53-537 on May 16, 1988)

Internal Office Registration Nos.	Japanese classification
6652 43	16C61

Procedural Correction

Date: November 8, 1978

Yoshikazu Kumagaya, Commissioner, Patent Office

1. Case No. 1976-127325

2. Title of the Invention

Method for Producing High-Purity Terephthalic Acid

3. Party Making the Amendment

Relation to the Case: Applicant

(315) Toray Industries, Inc.

2, Nihonbashi-Muromachi 2-chome, Chuo-ku, Tokyo-to

4. Date of Amendment Order

Voluntary

5. Subject of Amendment

"Detailed Description of the Invention" and "Brief Description of the Drawings" of the

Specification

6. Amendment Details

(1) The "number of days of washing" on line 22 of page 4 of the translation will be corrected to "washing frequency."

(2) The " When the procedure was repeated ten times, after 65.8 parts of the liquid from the reactor slurry that had been separated into solid and liquid fractions and then dehydrated, was added in place of the 71 parts of fresh acetic acid, the quality of the TPA product had all but stabilized, and the alkali transmissivity was 76%" on lines 3-6 of page 8 of the translation will

be corrected to "65.8 parts of liquid from the reactor slurry that had been separated into solid and liquid fractions and then dehydrated were added in place of the 71 parts of fresh acetic acid. When the above-mentioned procedure was repeated ten times, the quality of the TPA product had all but stabilized, and the alkali transmissivity was 76%."

5 (3) The "per one day" on lines 6-7 of page 8 of the translation is amended to read "per procedure."

 (4) The "7. washing machine" on line 4 of page 9 of the translation is amended to read "7. washer."

 (5) The "15. condensing machine" on line 8 of page 9 of the translation is amended to read
10 "15. condenser."